THE DEVELOPMENT OF A METHOD FOR THE MEASUREMENT OF THE HEAT CAPACITIES OF SOLIDS AT ELEVATED TEMPERATURES

A THESIS

Submitted in partial fulfillment of
the requirements for the Degree
of
Master of Science
in
Chemistry

by

James Holmes

Georgia School of Technology
Atlanta, Georgia

1938

ACKNOWLEDGEMENT

I wish to express my very great appreciation to Dr. W.M.Spicer for the suggestion of this problem and for his helpful advice and criticism during the course of the investigation.

I should also like to express my appreciation to Dr. C.E.Trimble and the Georgia Experiment Station for the use of certain materials needed in this research.

Approved June 1, 1938

TABLE OF CONTENTS

INTRODUCTION

Heat capacity data are of very great importance in determining free energy values and other important thermodynamic quantities. Consequently, the accurate determination of heat capacity data has long been one of the foremost problems of experimental chemistry. All calorimetric methods for determining specific heats involve the measurement of a temperature change. In spite of the apparent simplicity of such a determination, calorimetric measurements are considerably complicated by the tendency of heat to flow into or out of the apparatus. According to White[1] this complication is three-fold: (1) the need to calculate the loss or gain of heat by the system, (2) the apparatus must be such that all irregularities in the gain or loss of heat by the system are minimized as much as possible, (3) miscellaneous errors in the conduction and radiation of heat to and from the system . Of these three sources of error the first two are the more important since the third may be largely eliminated in several ways. For example, if the same procedure is used in making measurements as was used in the initial calibration of the apparatus, these miscellaneous errors will tend to be cancelled.

The first two sources of error were very large in the early methods for determining heat capacities. This fact is well indicated from a brief study of one of the earliest and at that time most sensitive instruments,

---

1) J.A.C.S., 40 , 1858, (1918)

namely, the Bunsen ice calorimeter.[1] In this method the sample was heated to the desired temperature in a crucible and then dropped into a cavity in a block of ice, after which a cover of ice was placed over the cavity. The determination of the specific heat involved a measurement of the amount of liquid formed. The method was based on the principle that a definite mass of solid in changing to liquid at a constant temperature absorbs a definite amount of heat. An accurate determination of the amount of heat absorbed by the block of ice was difficult due to the impossibility of removing the liquid adhering to the walls of the cavity. Another source of error was involved in the measurement of the temperature of the heated crucible. At the time this method was introduced thermometric measurements were still very crude and the most accurate determinations of temperature were through the use of an ordinary mercury thermometer.

One of the oldest and most fundamental methods for measuring heat capacities at high temperatures is known as the method of mixtures. The principle involved is that the sum of the heat lost by the hot bodies is equal to that gained by the cold. In practice the solid sample is heated in a crucible to a definite temperature and then dropped into the calorimeter which contains a liquid, such as water, of known mass and temperature. The gain of heat by the calorimeter is found by measuring its temperature rise and from this the specific heat may be calculated. There are two essential sources of error involved in the use of this method.

---

1) Bunsen, Phil. Mag., 41 , 161, (1871)

These errors are caused by the evaporation of the liquid used in the calorimeter and by heat gained through the necessary stirring of the liquid to maintain uniform temperature throughout. In order to eliminate these errors, elaborate and complicated apparatus have been devised involving the use of specially designed frictionless stirrers and high boiling calorimetric liquids. White[1] has probably developed the most efficient apparatus using this method. It is claimed that all errors due to splashing and evaporation have been eliminated through the use of Flato's cup, knocked under the surface of the water by the specimen falling into it and a spring shutter closing the calorimeter top.

The only other methods that have found very wide use in the measurement of specific heats at elevated temperatures are those involving the use of aneroid calorimeters. The first mention of such a calorimeter in the literature seems to have been made by Nernst[2] and his co-workers. They used an all-metal calorimeter composed of copper bearing two thermoelements and was contained in a vacuum tube. The success of the method depended upon the excellent thermal conductance of the metal to equalize the temperature in place of the stirring of a liquid. Outside this tube was another copper tube bearing a thermoelement. The whole was immersed in an ice bath and allowed to reach an equilibrium temperature throughout. The substance under investigation is heated to the desired temperature in a silver capsule and dropped into the block. From the difference

---

1) J.A.C.S., 55 , 1047, (1933)

2) Sitzb.kgl. preuss. Akad, Wiss., 12,13, 247-261, (1910)

---

in temperature of the two blocks and the temperature of the heated sample the specific heat was determined. It became evident at once that such a method was not only capable of considerable precision but was also applicable to a wide range of temperatures and to a wide range of investigations which could hardly be attained with any other single type of apparatus. As compared with the method of mixtures, for instance, there is no correction needed for the evaporation of the calorimetric liquid or due to the energy supplied by stirring. In recent years the very highest precision has been attained with this method by Jaeger[1] and his co-workers. In his most recent type of apparatus an accuracy of 0.3% is claimed to temperatures as high as 1650°C.

In spite of its numerous advantages the preceding method has one troublesome disadvantage, namely, that after several runs the crucible becomes battered and no longer makes the best possible contact with the calorimeter block. The present investigation was initiated as an attempt to overcome this difficulty by substituting a finely divided metal of high thermal conductivity for the metal block. It was decided to measure the specific heat of red lead monoxide over the range 150-250°C. in continuation of the investigations of Spencer and Spicer[2] who have measured its specific heat over a higher temperature range.

---

1) Rec. trav. chim., 47 , 513 (1928)

2) Unpublished Dissertation - Spencer and Spicer, U. of Virginia (1936)

PREPARATION OF LEAD MONOXIDE

Hydrated lead monoxide was prepared according to the method of Pleisner[1]. Barium hydroxide[2] was added slowly to a fresly prepared solution of lead acetate. The resulting hydrated oxide was washed ten to fifteen times with distilled water and then converted over to the red lead monoxide by the method devised by Spencer and Mote[3]. The hydrated oxide was placed in a flask and a saturated solution of sodium hydroxide was then added to it. The mixture was then heated to boiling over an air bath and at this temperature was rapidly converted to the red modification. The sodium hydroxide was removed and the oxide washed twelve or fifteen times by decantation with hot distilled water. The oxide was dried for a number of days over concentrated sulfuric acid in a desiccator. This proved a very effective method of drying since the oxide lost only a few milligrams upon being heated to 120°C for several hours in an oven and lost very little additional weight upon being later heated to over 250°C. A small portion of the prepared sample was heated to over 400°C and its failure to lose more than a few additional milligrams weight indicated the absence of appreciable amounts of carbonate, which Brill[4] claims is completely decomposed in the atmosphere at 337°C.

---

1) Arb. kais. Gesundh., 26 , 384, (1907)

2) All reagents are Baker Analysed C.P. reagents unless otherwise indicated.

3) J.A.C.S., 54 ,4618, (1932)

4) Z. phys. Chem., 57 , 736, (1907)

APPARATUS

The apparatus shown in the accompanying diagram was constructed with the following requirements in mind upon which the success of the method depends:

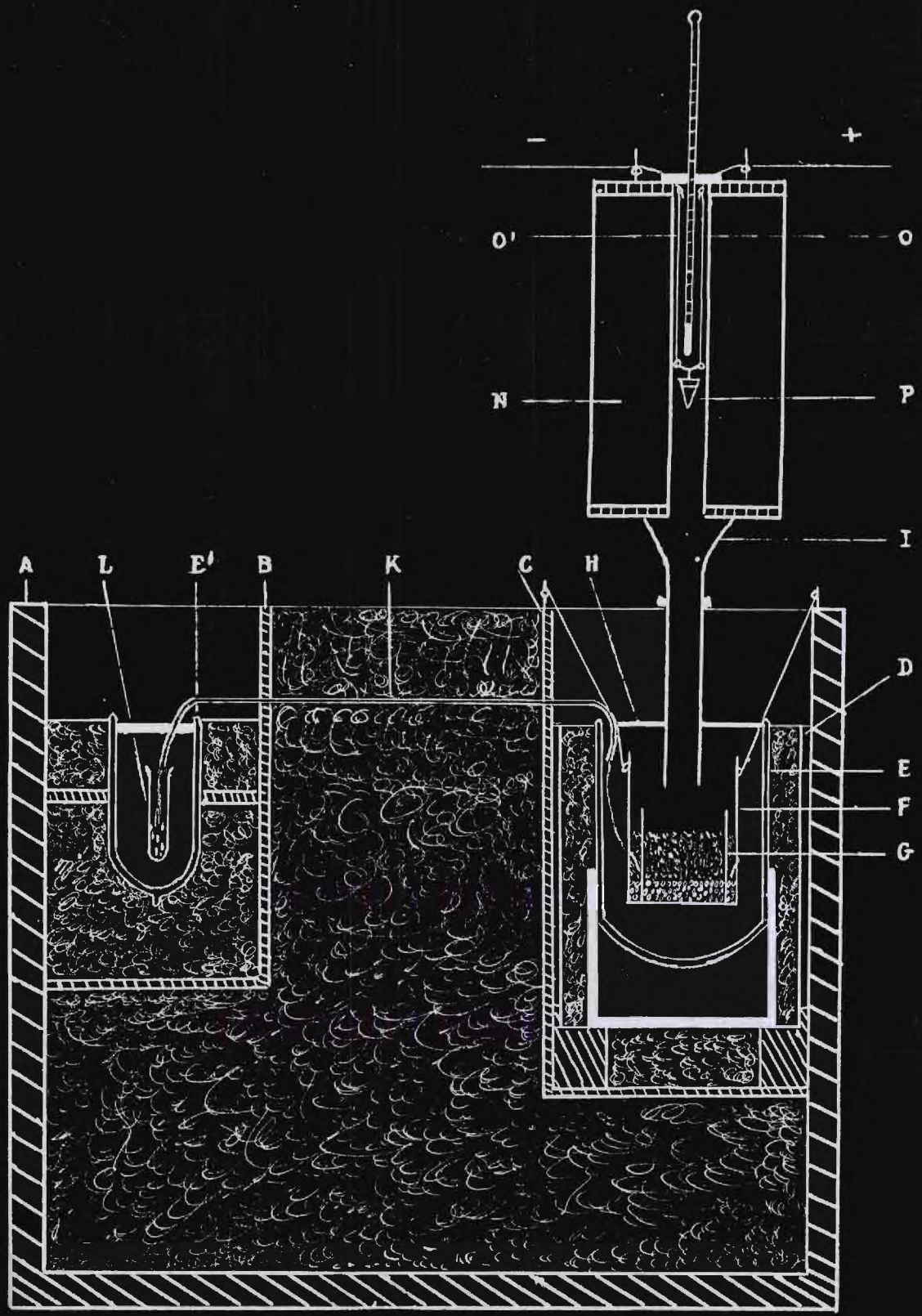
1) Keeping the environment of the calorimeter at constant temperature so that the rate of cooling of the calorimeter will be uniform.

2) Being able to measure accurately the temperature of the calorimeter.

3) Knowing the original high temperature of the crucible.

These specifications were not too rigidly followed in this particular investigation since the primary purpose was to test the validity of the method, leaving improvements necessary for the attainment of maximum precision to future investigations. It will be suggested how these requirements may be as closely approximated as by any other aneroid calorimeter in a later section.

As shown in the diagram, the apparatus consists of a large thick wooden box, A , whose dimensions are 17'' X 18'' X 20''. B and C represent two wooden partitions rigidly attached at the extremities of the box. D is a cylindrical card-board container snugly wedged into its position in which a large Dewar flask, E , is placed. The space between the walls of the Dewar flask and the card-board container is insulated with cotton. The calorimeter, F , is suspended in the Dewar flask being supported from the upper framework of the box. It consists of a cylindrical tube of sheet aluminum closed at one end partially filled with a mixture of aluminum powder and 20-mesh aluminum granules. Aluminum was chosen as the calorimetric metal because of its high thermal


−
+
O'
O
N
P
I
A
L
E'
B
K
C
H
D
E
F
G

conductivity and because a higher temperature rise results per unit volume due to the relatively low density of this metal as compared with other suitable metals. The granular aluminum was added to check the fall of the crucible[1] being placed at the bottom of the calorimeter and covered with sufficient aluminum powder to insure complete burying of the crucible. A tube, G , likewise of sheet aluminum was inserted in the calorimeter at a distance of about half an inch from the outer tube. The purpose of the inner tube is to shield the thermocouple junctions from damage due to contact with the falling crucible. The outer calorimeter tube contains nine small holes at equidistant points in a circle around it through which the junctions of the thermocouple were inserted. These junctions were buried to a suitable depth in the powder filling the space between F and G. The leads were then soldered with rosin in a fixed position in the calorimeter. The individual leads were then gathered into a compact bundle and passed through a small hole in the tight-fitting cork stopper, H , provided for the Dewar flask. This stopper also contained a large circular hole in the center through which a cylindrical glass shaft, I , could be inserted. The bore of this shaft was such that the crucible made a snug fit as it passed through and was directed in the same direction with each successive drop. The shaft was so constructed that it reached from the furnace to within an inch or so of the powdered

---

1) The crucible was constructed in the shape of a projectile to facilitate its burial and was of the highest quality of silver throughout. The upper diameter was 2.5 cm. and the overall length 5.5 cm. The volume of the crucible was approximately 10 cc. and its weight approximately 47 grams.

---

metal in the calorimeter. Since it was desirable to remove the shaft and to stopper the outfit as soon as the crucible had dropped, the shaft was constructed so that it could be supported in the desired position during the drop and easily removed afterward. This was accomplished by placing two wires several inches above the calorimeter sufficiently separated so that the shaft could be supported from them by means of a circular cork glued firmly to the shaft in the desired position. K represents a glass tubing containing the thermocouple and L is a small test tube holding the cold junctions of the couple and is filled with paraffin. This test tube is suspended in a small Dewar flask, E' , which is firmly held in position in partition B as already mentioned. The whole box is filled with loosely packed cotton to insure satisfactory insulation and the partitions B and C are so constructed that the cotton can be placed to a height of six or seven inches above the Dewar flasks. As a final measure of precaution the whole apparatus was covered during the run with a heavy strip of insulating material. Thermocouple leads run from the hot and cold junctions to a potentiometer which is used to measure the temperature difference between the two junctions.

The furnace, N , in which the crucible was heated is an ordinary Hoskin's circular furnace, type FD303. It was rigidly attached in an upright position to a fixed framework support. The furnace was provided with an asbestos stopper for the bottom and an especially designed soapstone cover for the top. Thick copper leads extended from a rheostat to the furnace support and were rigidly attached immediately above the furnace in such a position that two similar leads, O and O' , could be easily fastened to them. At the lower extremities of O and O' the crucible, P , containing the sample was suspended by means of a small piece

of copper wire (No. 36 gauge) to the thick leads by means of a ring on the top of the crucible constructed for this purpose. The top of the crucible was firmly attached to the crucible proper by means of bayonet joints. A 360°C thermometer was suspended in the furnace from a fixed over-head support. The insulating cover was constructed with grooves in such a position that it made a snug fit about the thermometer and the leads when it was moved into position. When the switch was closed the fine wire holding the crucible was instantly fused and the crucible descended through the shaft into the calorimeter. After the crucible was in the calorimeter, the box was quickly moved away from the furnace, the glass shaft removed, the opening into the calorimeter closed with a cork, and the partition filled with cotton. According to Jaeger and Rosenbohm[1], the heat loss in falling so short a distance is negligible, especially since the first, and consequently the slowest part of the descent takes place in the furnace. The temperature of the furnace was carefully regulated by means of several rheostats connected in series.

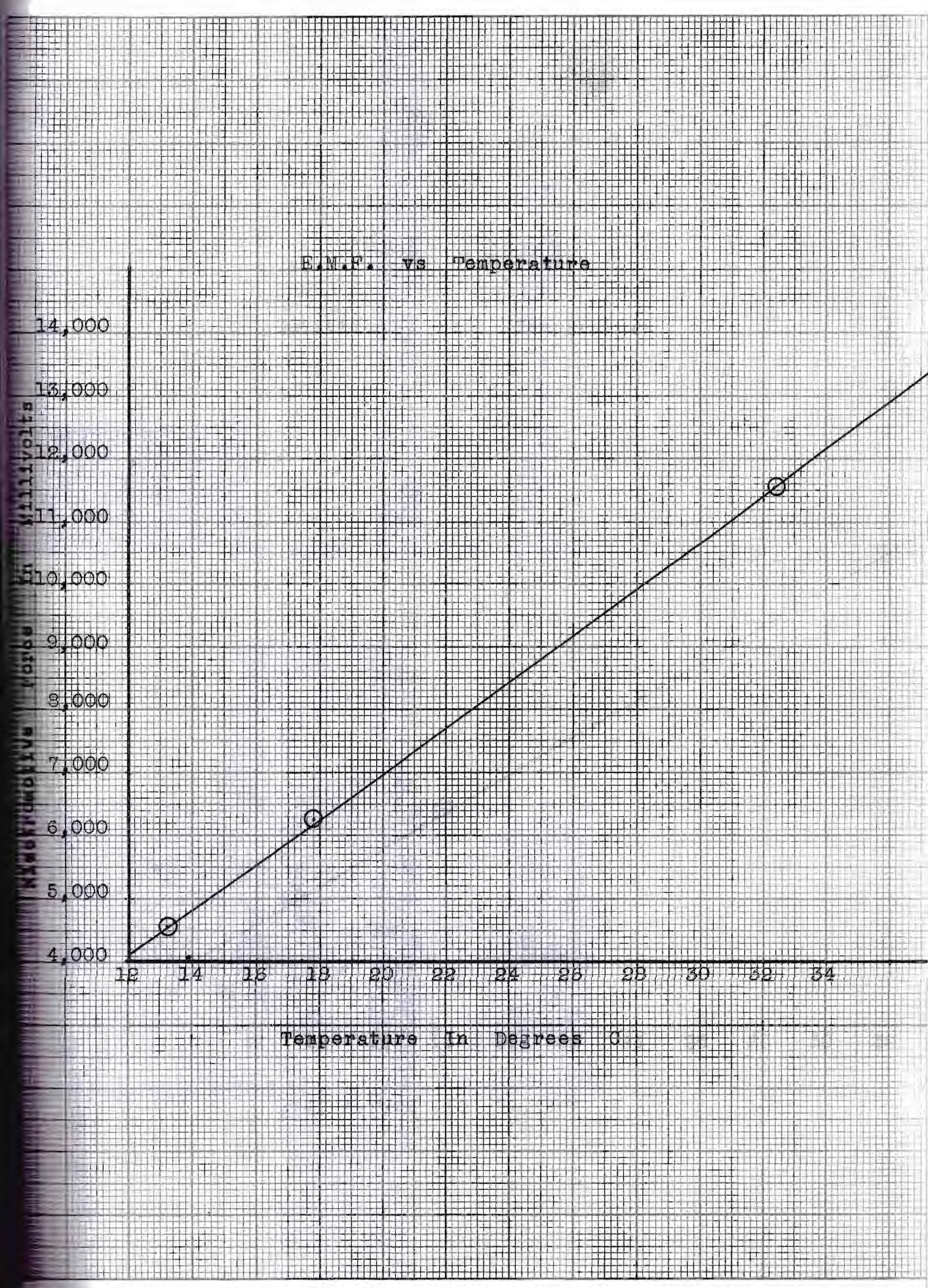
The equipment for measuring the electromotive force of the thermo-element consisted of a Leeds and Northrup[2] Student potentiometer and a Leeds and Northrup[3] horizontal pointer-scale type galvanometer. The working standard cell was a new one and had been just previously certified by the Eppley laboratory. After the completion of this investigation it

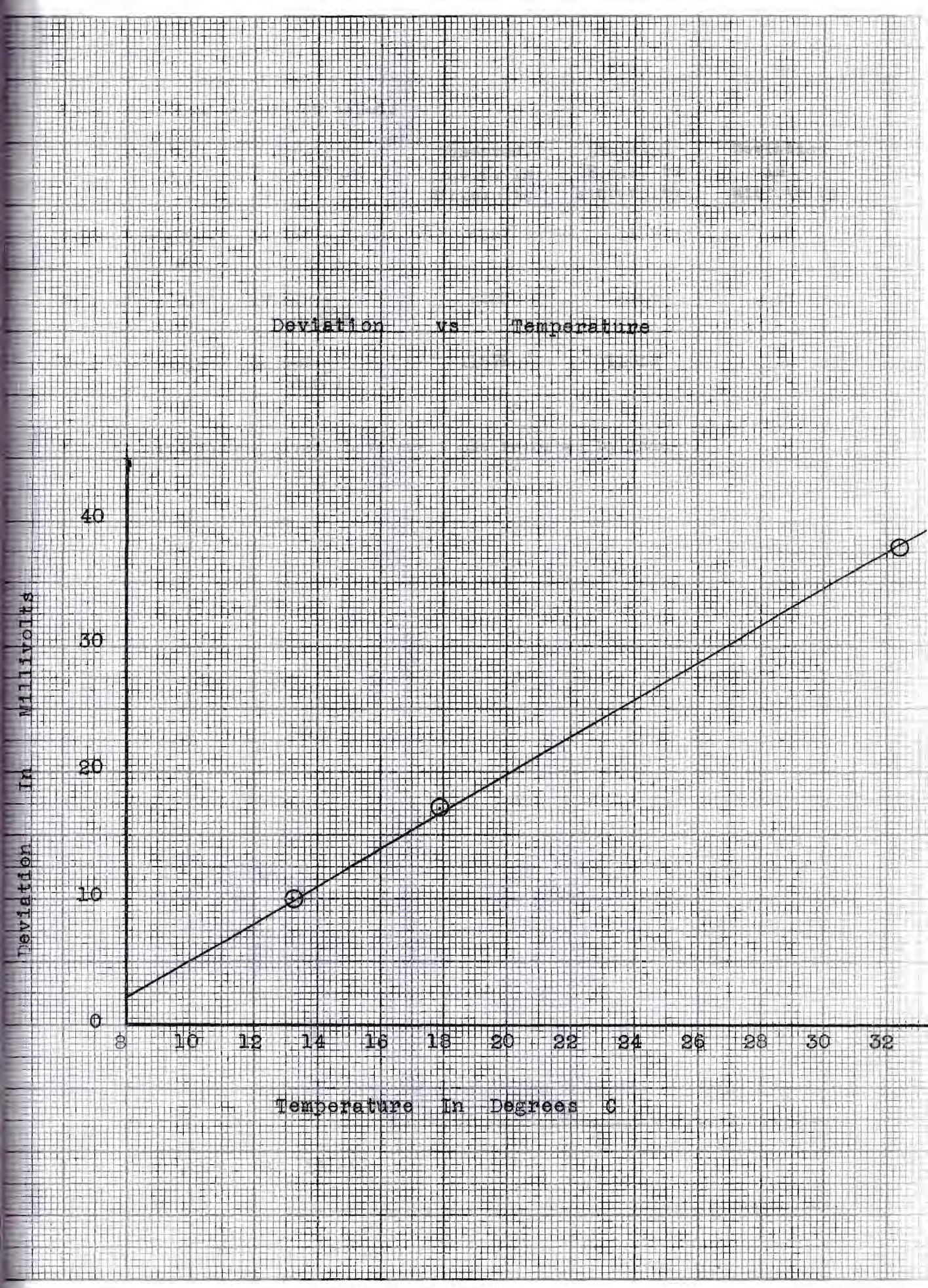
---

1) Rec. trav. chim., 47 , 513 (1928)

2) Catalog No. 7651

3) Catalog No. 11-506-28


E.M.F. vs Temperature
14,000
13,000
12,000
11,000
10,000
9,000
8,000
7,000
6,000
5,000
4,000
Millivolts
12
14
16
18
20
22
24
26
28
30
32
34
Temperature In Degrees C


Deviation vs Temperature
Deviation In Millivolts
0
10
20
30
40
8
10
12
14
16
18
20
22
24
26
28
30
32
Temperature In Degrees C

following results were obtained:

Substances	Constant Temperature	Observed E.M.F. in Microvolts	Standard E.M.F. in Microvolts	Deviation in Microvolts
$NaNO_3$ + Na_2SO_4. 10 H_2O	13.154 ± 0.0011	4582	4590	8
NaCl + Na_2SO_4. 10 H_2O	17.878 ± 0.0022	6283	6300	17
Na_2SO_4. 10 H_2O	32.383 ± 0.001	11572	11610	38

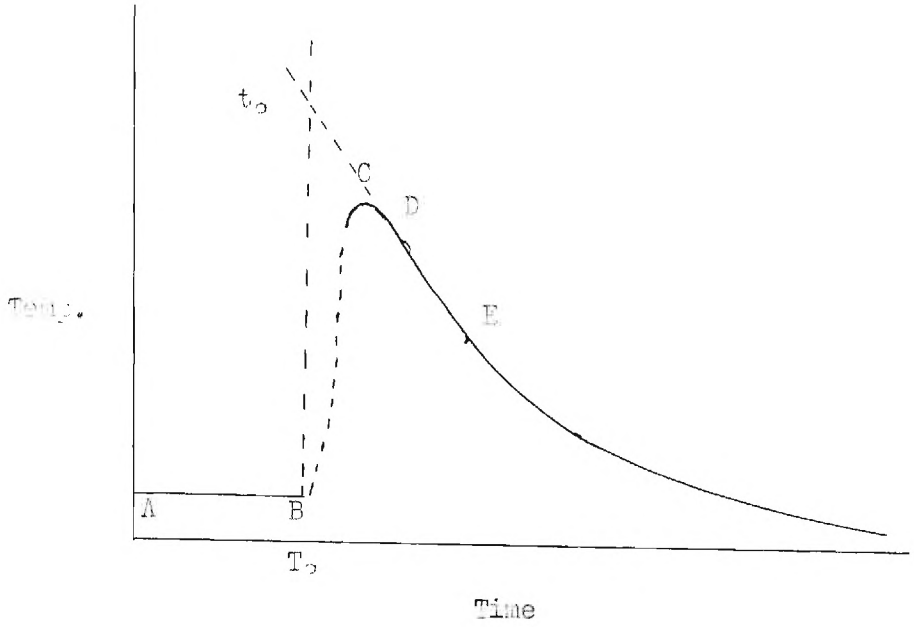
The Standard values given above are those reported by Adams[1].

---

1) J.A.C.S., 36 , 65, (1914)

THE METHOD OF CALCULATION

A plot of a typical run is shown in the accompanying figure. t is the difference in temperature between the hot and cold junctions of the thermocouple. This is also the temperature of the calorimeter since the cold junction is at 0°C. The symbol T represents the time in minutes. The por-



tion of the curve AB represents the constant temperature equilibrium attained by the system before the crucible is dropped at time T_o. On dropping the heated crucible into the calorimeter, the temperature, as shown by the electromotive force readings of the thermocouple, rises quickly to a maximum, C , in about four to five minutes, and then falls off along the curve CDE. It is now necessary to determine t_o, which represents the temperature to which the calorimeter would have risen if there had been instantaneous transfer of heat from the crucible. The calorimeter as a whole (the metal tube, powdered aluminum, and Dewar flask) never reached

t_o since the thermocouple is not at the center of the calorimeter and consequently some heat is lost through radiation. After the first rapid heat transfer has been completed and the heat has been uniformly distributed through the calorimeter, the cooling proceeds along DE. The point D is reached when a uniform temperature gradient has been established in the calorimeter. In order to determine t_o, it is obviously desirable to extrapolate the portion of the curve DE since this is the first portion of the curve representing a constant cooling of the calorimeter. When the cube root of the electromotive force is plotted against the temperature the resulting curve is easily extrapolated since it very closely approaches a straight line. The accuracy of such an extrapolation was estimated to be approximately 0.1- 0.2 per cent.

CONDUCT OF A RUN

After the system had reached a constant temperature, the crucible was suspended in the furnace and heated for at least fifteen minutes at the desired temperature[1], the box moved under the furnace, the crucible dropped, and the time of dropping recorded. The box was immediately moved from under the furnace and the heating of the furnace discontinued. The glass shaft was quickly removed, a cork stopper being inserted in its place and the whole partition filled with cotton. This entire procedure occupied several minutes after which readings of the electromotive force were taken every minute for seventy minutes. During this time readings were taken every four minutes against the standard cell to make certain that there were no fluctuations. Having found the value of t_o by extrapolation, the temperature rise of the calorimeter, Δt, was obtained. The subsequent procedure would depend upon whether the run were a calibration or an actual measurement of the specific heat of an unknown. If it were a calibration, the amount of heat given to the calorimeter by the crucible alone would be divided by Δt to obtain W, the water equivalent of the calorimeter. When the heat capacity of an unknown was being measured, Δt would be multiplied by W to obtain the heat given up to the calorimeter by the sample and the crucible. By subtracting from this value the amount of heat given up by the crucible alone, the heat given up by the sample would be obtained.

---

1) The temperature was maintained constant ($t \pm 0.5°C$) as indicated by readings taken every minute on a 360° calibrated thermometer.

CALIBRATION OF THE CALORIMETER

In order to obtain the water equivalent , W , of the calorimeter,it was necessary to calibrate it with a solid whose heat capacity is well known. For this purpose, it was found very convenient to use the empty crucible itself since the heat capacity of silver has been determined with an accuracy estimated to be at least 0.5% by Eastman, Williams, and Young[1] . They give as the total amount of heat given up per mole of silver in falling from t' to 20°C

$$Q'_o = -138.5 + 6.02\ t' + 0.00076t'^2 \qquad \text{Equation (1)}$$

This equation holds for upper temperatures between 100-900°C. In order to obtain the heat given up per mole of silver between 20°C and the calorimeter temperature t_o, the following equation obtained by Eastman, Williams, and Young[1] for the specific heat of silver was used.

$$C_p = A + Bt \qquad \text{Equation (2)}$$

A = 25.1 joules per gram atom and B = 6.03 x 10^{-3} joules per gram atom. Since this equation is valid over the range 0-961°C, we are able to integrate it from 20°C to the calorimeter temperature, t_o , as follows:

$$\int_{20}^{t_o} C_p\, \Delta t = Q_o = 25.1\ (t_o - 20) + 0.00302\ (t_o - 20^2) \qquad \text{Equation (3)}$$

The details of an actual run (number I) made during the calibration will now be given. The empty crucible, whose total weight was determined to be 47.0416 grams on an analytical balance, was suspended in the furnace. After the system had reached temperature equilibrium, the

---

1) J.A.C.S., 46 , 1181 (1924)

/

furnace was heated to the desired temperature (200 ± 0.5°C) and maintained at this temperature for fifteen minutes. Readings were taken every minute (stop watch) during this interval to make certain that the system had reached constant temperature before the crucible was dropped. The box was now moved under the furnace and the crucible dropped. The box was immediately moved from under the furnace, the shaft replaced by a tight-fitting stopper as previously described and readings taken again as indicated in the following table.

time	e.m.f. in μ v.
8:20:01	10,031
21:05	10,032
22:04	10,032
23:01	10,031
24:02	10,034
25:05	10,032
26:00	10,031
27:02	10,033
28:00	10,032
29:02	10,030
30:00	10,030
31:00	10,032
32:01	10,032

At this point the box was moved under the furnace and at 8:34:00 the crucible was dropped. After removing the box from beneath the furnace and having proceeded as already mentioned, readings were again taken as indicated.

time	e.m.f. in μ v.
8:36:15	12,326
37:02	12,790
38:02	13,124
39:01	13,270
40:00	13,375
41:03	13,362
42:03	13,344
43:11	13,304
44:00	13,271
45:05	13,227
46:00	13,180
47:00	13,132
48:03	13,082
49:02	13,045
50:01	12,997
51:03	12,952
52:02	12,920
53:04	12,862
54:01	12,844
55:00	12,793
56:00	12,765
57:02	12,734
58:01	12,696
59:04	12,670
9:00:00	12,644
01:02	12,617

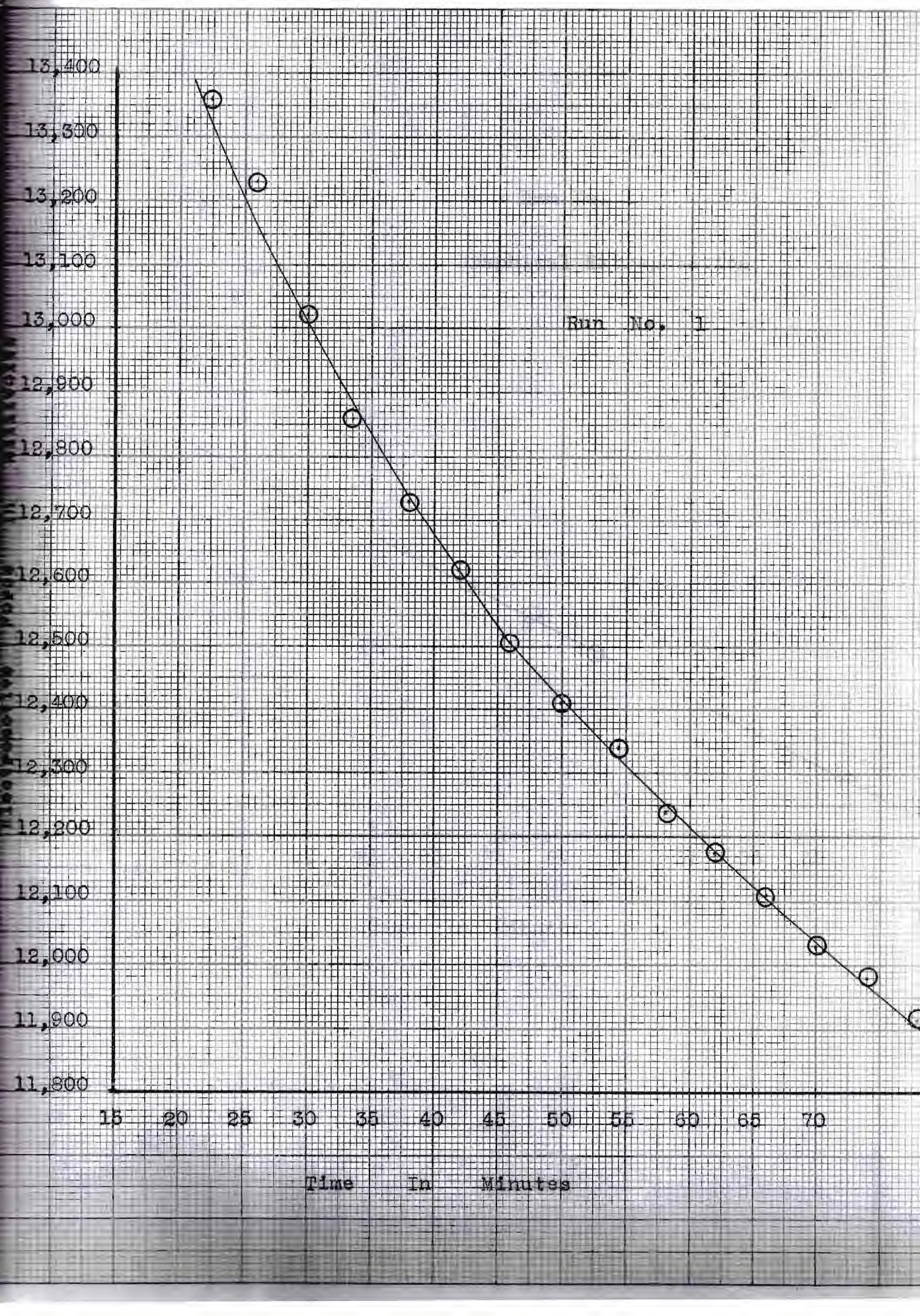
time	e.m.f. in μ v.
9:02:08	12,590
03:00	12,564
04:01	12,531
05:04	12,506
06:11	12,484
07:02	12,450
08:00	12,428
09:03	12,410
10:00	12,390
11:04	12,378
12:02	12,360
13:05	12,334
14:01	12,320
15:00	12,295
16:01	12,284
17:00	12,245
18:02	12,227
19:08	12,220
20:00	12,205
21:02	12,175
22:05	12,161
23:02	12,135
24:02	12,106
25:02	12,084
26:03	12,060
27:01	12,046

time	e.m.f. in μv.
9:28:00	12,029
29:04	12,014
30:00	11,994
31:00	11,986
32:03	11,980
33:02	11,955
34:04	11,931
35:01	11,928
36:00	11,915
37:08	11,904
38:02	11,871
39:02	11,870
40:02	11,841
41:00	11,826
42:04	11,810

In the accompanying graph, the values of the e.m.f. have been plotted against the time and the portion of the curve DE extrapolated in order to obtain t_o as mentioned previously. From this we find t_o = 38.3755. Since the original temperature of the calorimeter was 28.1403°C, we calculate that Δt = 10.2352°.

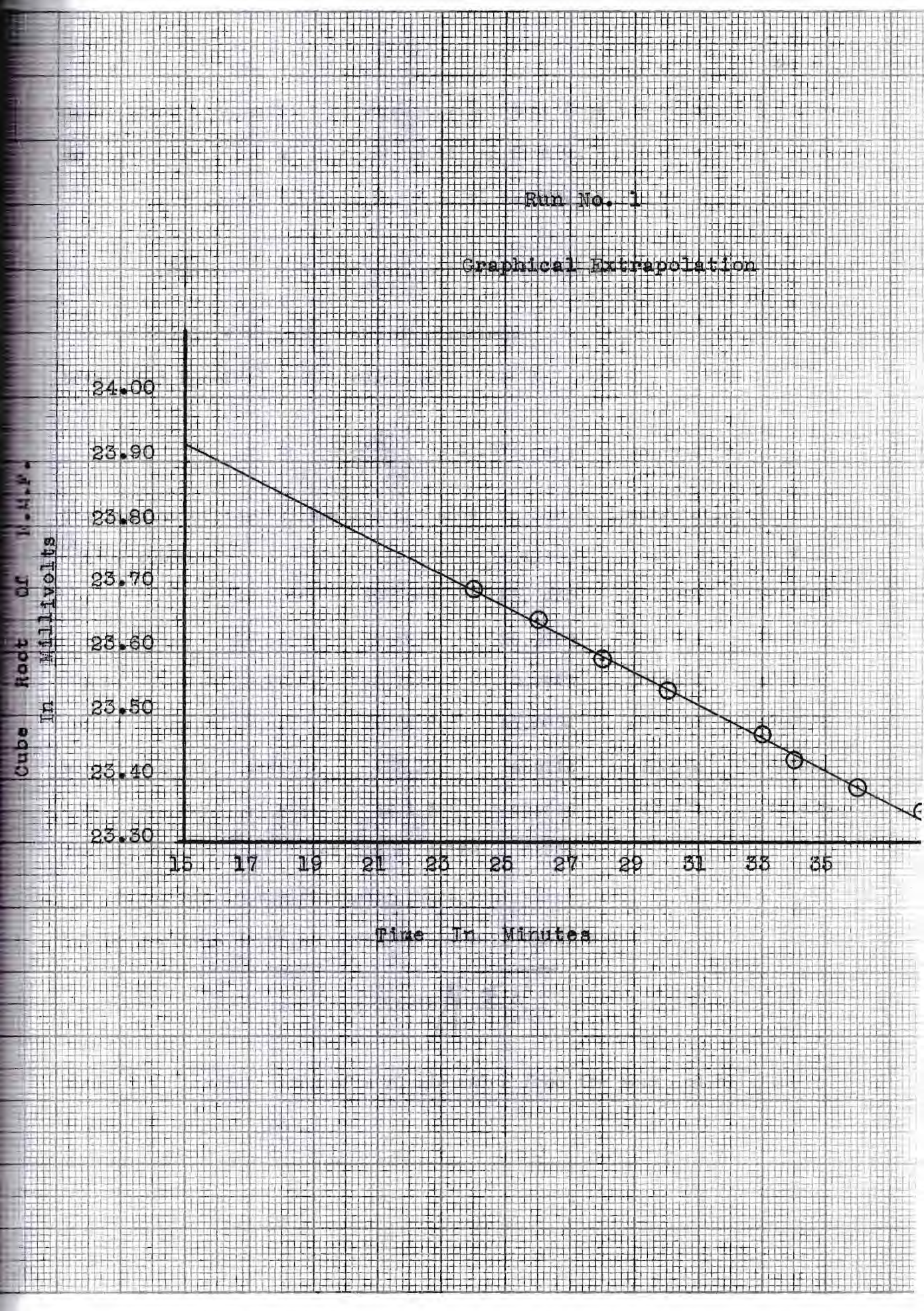
To obtain the heat given up by the crucible , t' = 200 is substituted in equation (1). This gives,

Q_o' = 1095.9 cal. given up between 200°C and 20°C. However, a correction must be made to this value since the crucible did not cool all the way to 20°C but only to t_o = 38.3755°C. We must therefore subtract


13,400
13,300
13,200
13,100
13,000
12,900
12,800
12,700
12,600
12,500
12,400
12,300
12,200
12,100
12,000
11,900
11,800
Run No. 1
15
20
25
30
35
40
45
50
55
60
65
70
Time In Minutes

Run No. 1

Graphical Extrapolation



Q_o as given by equation (3) where t = 38.3755, from the value of Q_o' given above. Substituting in equation (3) we find Q_o = 110.8 calories per mole.

$Q_o' - Q_o$ = 981.5 cal. per mole of silver, or

$$\frac{981.5}{107.88} = 9.1314 \text{ cal. per gram of silver}$$

9.1314 x 47.0461 = 429.60 calories,

total heat received by the calorimeter from the silver.

$$W = \frac{429.60}{10.2352} = 41.973 \text{ calories per degree.}$$

The results of the calibration are shown in the following table:

t' = 200°C	I	II	III	IV	V
t_o	38.3755	39.5509	39.9433	41.4964	38.3282
t	28.1403	29.4277	29.9490	31.2864	28.2077
Δ t	10.2352	10.1232	9.9943	10.2100	10.1205
Weight of Ag.=w	47.0461	47.0403	47.0374	47.0309	47.0178
w $(Q_o' - Q_o)$	429.60	426.32	425.16	423.42	429.21
W	41.973	42.113	42.560	41.471	42.410
Average W		42.105 $\pm$ 0.128 (0.30%)			

Here, and in the following pages, the value preceded by the mark $\pm$ is the probable error as given by the well known equation

$$\pm 0.6745 \sqrt{\frac{\Sigma d^2}{n(n-1)}}$$

where d is the deviation of a single value from the mean and n is the number of observations.

PRELIMINARY RUNS WITH ZINC

Before making runs on a sample of unknown specific heat it was believed advisable to test the accuracy of the method with a sample whose specific heat is well known. Zinc was chosen for this purpose since it is easily obtained in a pure state, and in addition its specific heat has been thoroughly investigated by Eastman, Williams, and Young[1]. Thirty mesh zinc of C.P. quality was used. To remove any possible oxide coating that might have formed the sample was washed several times in dilute hydrochloric acid and finally with hot distilled water to remove the last traces of acid.

The procedure for a run with the zinc was similar to that for a calibration. The calculations too were similar until Δt had been obtained. then Δt was multiplied by W to obtain the total amount of heat, H , delivered to the calorimeter. From this was subtracted the heat given up by the crucible,

$$\frac{(Q_o' - Q_o)\ 47.0261}{107.88} = I$$

where 47.0261 is the weight of the crucible and Q_o' and Q_o were obtained from equations (1) and (3), respectively. This difference,

$$H - I = K$$

is the heat given up by the sample of zinc in falling from t' to t and,

$$\frac{K}{\text{wt. of sample}} = h',$$

---

1) J.A.C.S., 46 , 1181, (1924)

is the heat given up per gram. The accuracy of the values obtained experimentally may be checked as follows.

The specific heat of zinc can be represented by the following equation over the range 0 - 300°C according to an investigation by Eastman, Williams, and Young[1],

$$C_p = 25.1 + 0.011\ t$$

The heat given up per gram of zinc in falling from a temperature t' in this range to a lower temperature t_o may be represented as follows:

$$\int_{t_o}^{t'} C_p\ dt = Q_o = 25.1 + (t' - t_o) + 0.0055\ (t'^2 - t_o^2)$$

The experimental values, the corresponding calculated values, and the per cent deviations are shown in the table below.

t' = 200°C	I	II	III
t_o	42.6750	43.1720	42.0560
t	28.3837	28.9647	27.7730
Δt	14.2913	14.2073	14.2830
H	601.66	598.13	601.31
I	417.95	416.63	419.43
K	183.71	181.50	181.88
Wt. of Zinc	14.2913	12.0162	12.0073
h (exp.)	15.260	15.105	15.148
h (calc.)	15.211	15.164	15.273
Per cent Deviation	0.33	0.33	0.79

---

1) Loc. cit.

HEAT CAPACITY OF RED LEAD MONOXIDE

The same procedure was followed with the oxide as has been described for the runs made with zinc. Due to the fact that there is a variation in t_o from run to run comparisons could be made best if the heat,h, given up per gram of sample between a high temperature t' and a fixed low temperature, say 25°C, were calculated. In order to do this it is only necessary to know the specific heat, C_p, of the oxide at 25°C, for

$$h' + C_p \Delta t = h$$

Randall and Spencer[1] give for the yellow lead monoxide

$$C_p = 11.25 + 0.0016\ T$$

Since no such data is available for the red oxide, and since the heat capacities of the two differ by only about 2%[2], the specific heat of the yellow may be used to correct the red oxide also. For T = 298.1°C, the above equation gives a value of $C_p = 0.0526$ cal. deg^{-1} $gram^{-1}$.

The heat given up per gram of red lead monoxide between t' and 25°C., and the average specific heat between these temperatures are tabulated in the following table.

---

1) International Critical Tables, First Edition
McGraw-Hill Co. Vol. VII, page 248

2) Loc. cit. (Spicer and Spencer)

$t' = 150°C$	I	II	III	IV
t_o	35.7058	35.0242	36.3983	33.1985
t	26.8318	26.0636	27.5019	24.1285
Δt	8.8740	8.9606	8.8964	9.0700
H	373.65	372.93	374.58	381.90
I	299.16	296.59	300.94	305.56
K	73.49	76.34	73.64	76.34
Wt. oxide	11.8503	12.2978	12.0257	12.0289
h'	6.2016	6.2076	6.1235	6.5463
$C_p \Delta t$	0.5631	0.5273	0.5996	6.5463
h	6.7647	6.7349	6.7235	6.7775

average h 6.7501 $\pm$ 0.0084 cal. $gram^{-1}$ (0.13%)

average C_p 0.0540 cal. $deg.^{-1}$ $gram^{-1}$.

$t' = 175°C$	I	II	III	IV
t_o	36.0283	37.0525	35.9853	38.5782
t	25.1178	26.2177	25.0700	27.8639
Δt	10.9105	10.8348	10.9133	10.7143
H	459.39	456.20	459.50	451.13
I	366.38	363.66	366.49	359.58
K	93.01	92.54	93.01	91.55
Wt. oxide	12.0224	12.0106	12.0119	11.9980
h'	7.7364	7.7050	7.7432	7.6301
$C_p \Delta t$	0.5801	0.6340	0.5777	7.6301
h	8.3165	8.3390	8.3209	8.3444

average h 8.3302 $\pm$ 0.0046 cal. $gram^{-1}$ (0.06%)

average C_p 0.0555 cal. $deg.^{-1}$ $gram^{-1}$.

$t' = 200°C$	I	II	III	IV
t_o	40.3928	37.6667	38.1936	38.8664
t	27.7457	24.8179	25.4010	26.1382
Δt	12.6471	12.8488	12.7926	12.7282
H	532.51	541.00	538.64	535.94
I	423.66	430.94	429.54	427.94
K	108.85	110.06	109.10	108.20
Wt. oxide	12.0339	12.0008	12.0055	12.0011
h'	9.0452	9.1710	9.0704	9.0160
$C_p \Delta t$	0.8097	0.6663	0.6940	0.7294
h	9.8549	9.8373	9.7644	9.7454

average h 9.8005 $\pm$ cal. $gram^{-1}$ (0.58%)

average Cp 0.0560 cal. $deg.^{-1}$ $gram^{-1}$.

$t' = 225°C$	I	II	III	IV
t_o	40.6409	37.4308	39.7473	38.4309
t	25.9519	22.5036	25.0190	23.6019
Δt	14.6890	14.9272	14.7283	14.8290
H	618.49	628.52	620.14	624.39
I	491.93	500.21	494.01	497.38
K	126.56	128.31	126.13	127.01
Wt. oxide	12.0011	11.9989	12.0114	12.0031
h'	10.5369	10.6943	10.5090	10.5818
$C_p \Delta t$	0.8227	0.6539	0.7757	0.7065
h	11.3596	11.3482	11.2847	11.2883

average h 11.3202 $\pm$ 0.0132 cal. $gram^{-1}$ (0.12%)

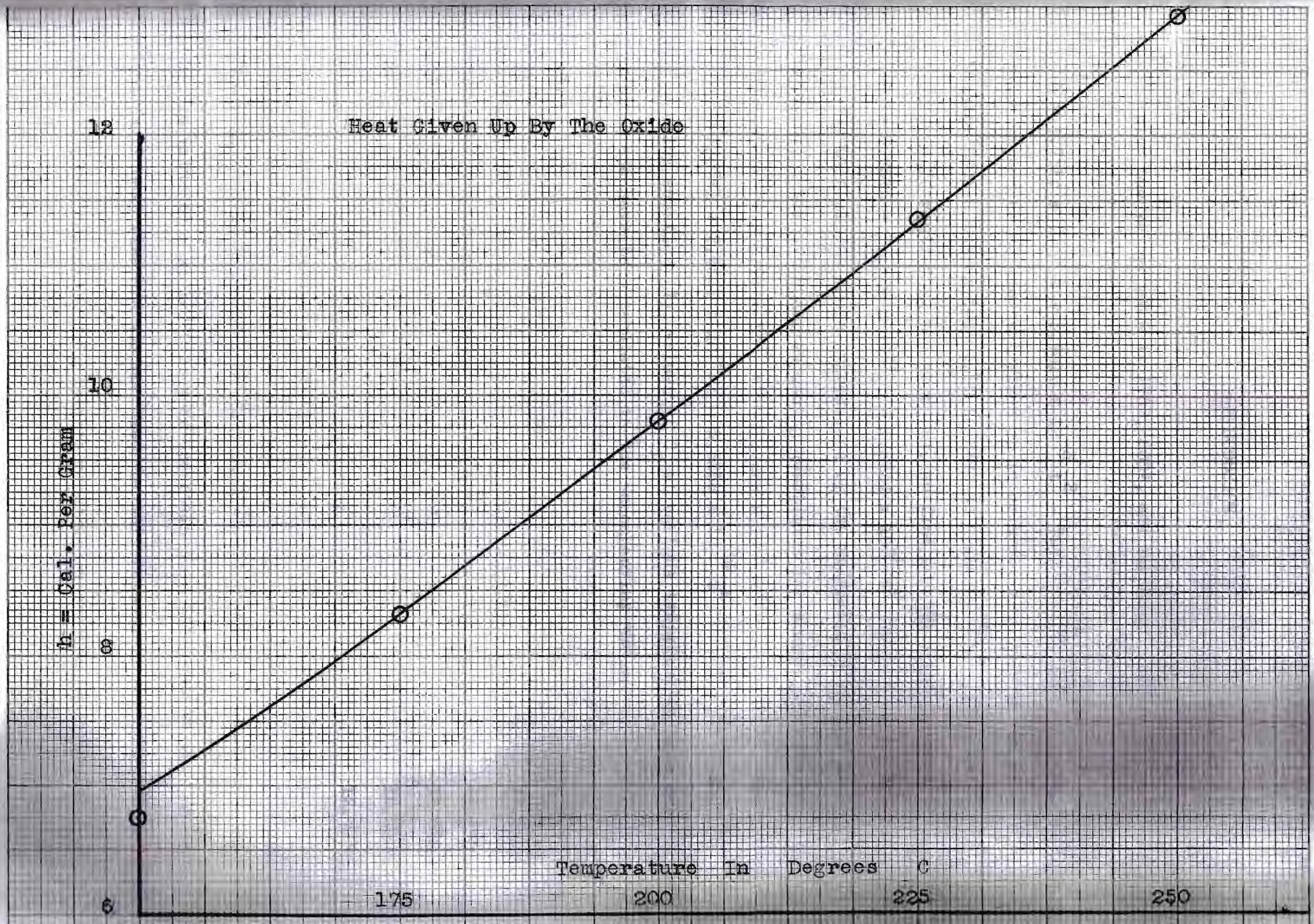
average C_p 0.0566 cal. $deg.^{-1}$ $gram^{-1}$.

$t' = 250°C$	I	II	III	IV
t_o	42.7250	40.8900	40.5909	40.8900
t	26.1062	24.1223	23.7817	16.7420
Δt	16.6188	16.7677	16.8092	16.7420
H	699.75	706.01	707.77	704.93
I	556.13	560.21	561.59	560.14
K	143.62	145.80	146.18	144.79
Wt. oxide	12.0028	11.9997	12.0077	12.0060
h'	11.9656	12.1503	12.1759	12.0599
$C_p \Delta t$	0.9323	0.8358	0.8201	0.8358
h	12.8979	12.9861	12.9960	12.8957

average h 12.9439 ± 0.0184 cal. $gram^{-1}$ (0.14%)

average C_p 0.0575 cal. $deg.^{-1}$ $gram^{-1}$.

On the following page h is plotted against t'.


Heat Given Up By The Oxide
12
10
8
6
h = Cal. Per Gram
Temperature In Degrees C
175
200
225
250

DISCUSSION

I. Results:

Using the values of h at 175°, 200°, and 250°C[1],

the equation

$$h = 3.7515 \times 10^{-2}\, t + 5.9016 \times 10^{-5}\, t^2 - 7.8971 \times 10^{-9}\, t^3 \qquad \text{Eq. (4)}$$

which expresses h, the heat given up in calories per gram of red oxide in falling from a temperature t_o°C to 25°C as a function of t, was derived.

By differentiating equation (4), we find for the specific heat,

$$C_p = 3.7515 + 1.1803 \times 10^{-4}\, t - 1.5794 \times 10^{-8}\, t^2 \qquad \text{Eq. (5)}$$

By multiplying these expressions by the molecular weight of lead monoxide, 223.22, the corresponding quantities for a mole are obtained:

$$H = 8.3741 + 1.3174 \times 10^{-2}\, t^2 - 1.7628 \times 10^{-6}\, t^3 \qquad \text{Eq. (6)}$$

$$C_p = 8.3741 + 2.6348 \times 10^{-2}\, t - 3.5256 \times 10^{-6}\, t^2 \qquad \text{Eq. (7)}$$

Using equation (7), values of C_p at various temperatures were calculated and have been tabulated in the accompanying table.

t°C	C_p
150	11.5330
175	11.9053
200	12.2335
225	12.5176
250	12.7576

---

1) The value of h at 150°C is more uncertain than the other values due to the small heat rise and was not used for this reason.

On the following page these values of C_p have been plotted against the temperature.

In deriving equation (4) for h , it was only necessary to use three of the five values of h obtained at different temperatures. The value of h at 225°C as calculated from the empirical equation (4) is compared to the observed value below.

t	calculated h	observed h	% difference
225°C	11.3386	11.3202	0.16

II. Apparatus:

The apparatus which has been described has been used for measuring the heat capacities of solids in the range 150-250°C and could easily be extended to temperatures as high as 500-600°C. The upper limit could be extended even further by the use of a powdered metal of high thermal conductivity whose melting point is considerably higher than that of aluminum. The lower limit could probably be extended to 100°C but for further extension the present small crucible would not be satisfactory since there would not be a large enough temperature rise in the calorimeter.

For more accurate measurements than those which have been obtained above, several desirable modifications are suggested. They are:

1) The use of a powdered metal of higher thermal conductivity than aluminum such as copper or silver.

2) The use of a thermocouple to measure the furnace temperature more accurately.

3) The provision of a more constant temperature environment than the

air such as an oil thermostat.

4) The addition of a spring top to the calorimeter controlled by a sensitive trigger such that the falling crucible could trip this trigger releasing the top, and this being driven by a strong spring could close very quickly over the calorimeter. Such a device would make any loss of the powdered metal through spraying entirely negligible.

SUMMARY

1) A new type of aneroid calorimeter is described for measuring the heat capacities of solids at high temperatures. Improvements in the apparatus for more accurate measurements over a wide range of temperatures are suggested.

2) The validity of the method was demonstrated by numerous runs made on zinc in which the experimental values for the heat capacity were compared with the calculated values. The per cent deviation between these two sets of values was calculated to be only 0.48%.

3) An empirical expression for the heat given up by red lead monoxide between a temperature t in the range 150-250°C as a function of t is derived from the experimental data. By differentiating this expression an equation giving the true heat capacity of the oxide over the range 150-250°C is derived.